NOVEL TRANSITION METAL COMPOUNDS WITH PROMISING THERMOELECTRIC PROPERTIES

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Progress in the search for new high temperat ure thermoelectric materials at the Jet Propulsion I aboratory is reviewed, Novel transition metal compounds were selected as potential new high performance thermoelectric materials and criteria of selection arc presented and discussed. Samples of these new compounds were prepared at JPI, by a variety of techniques. Encouraging experimental results obtained on several of these compounds arc reported and show that they have the potential to be the next generation of thermoelectric materials.

INTRODUCTION

The thermoelectric technology only occupies a niche market although its reliability, simplicity and long life time compare, to the other energy conversion technologies. I ow efficiency of the thermoelectric materials is the main reason for the actual small number of practical applications. State-of-the-art thermoelectric materials used in the actual devices, such as Bi_2Te_3, PbTe and SiGe, were identified in the 1950's and although extensive theoretical and experimental studies have resulted in substantial improvements of the properties of these thermoelectric materials, dimensionless figure of merit ZT values hardly exceed 1, as illustrated in Figure 1. No theoretical limit has been established on the dimensionless figure, of merit ZT [1]. Several options can be considered to improve ZT. One of them is to look at new binary and ternary compounds or alloys. It has also been recently predictted that the thermoelectric figure of merit of thin-films and quantum wells can be significantly larger than conventional thermoelectric materials [2].

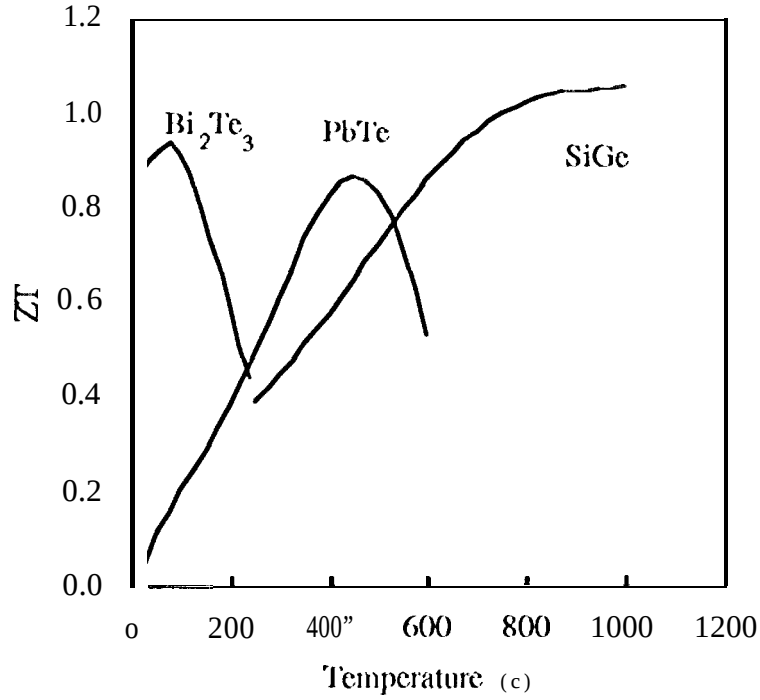

Figure 1, Dimensionless figure of merit as a function of temperature for selected n-type alloys.

A new approach was recently started at the Jet l'repulsion Laboratory (JPL) to look at novel compounds and alloys [3]. Several Si-rich transition metal silicides were first studied including Ru_2Si_3, a high temperature refractory semiconductor with a good potential for a high figure. of merit [4]. The isostructural germanide, Ru_2Ge_3, was also recently investigated [5]. This paper reports progress on the search for new thermoelectric materials currently underway at J]>]., The criteria for the selection of novel compounds and alloys arc presented and discussed. Thermoelectric properties obtained for several transition metal (group VIII) compounds with elements of column V are presented.

SELECTION OF NEW THERMOELECTRIC MATERIALS

According to Ioffe [6], the figure of merit of a thermoelectric material can be related to fundamental parameters by defining a parameter $\beta = p\left(\frac{m^*}{m_0}\right)^{3/2}/\lambda_R$, where m* is the dmsity-of-states

effective mass, m. the free electron mass, μ the carrier mobility and λ_R the lattice thermal conductivity. For a particular temperature of operation, the band gap (E_g) should be greater than $4k_BT$ in order to avoid the activation of the minority carriers which quenches the Seebeck coefficient. Unfortunately, there are many known compounds whose mobility, effective masses, band gap and lattice thermal conductivity have never been measured and Ioffe's rule is of little help for selecting new thermoelectric materials. However, Ioffe's rule obviously indicates that high-Z-value thermoelectric materials should have a low lattice thermal conductivity and a high carrier mobility and effective mass.

It has been shown that high carrier mobility can be more likely achieved in semiconducting compounds with low electronegativity difference (δx) between the elements in the compound [7]. A compound with a (δx) greater than 1 is most unlikely to have a mobility greater than 1000 $cm^2/V.s$. [7], The carrier mobility is mainly governed by the band structure and the interactions with the lattice vibrations and ionized impurities. in a covalently bonded material associated with low (δx) values, them interactions are lower compare to more ionic lattices where the Coulomb scattering tends to be increased, thus decreasing the carrier mobility. Consequently, ncw thermoelectric materials should be selected among low (δx) compounds, at least lower than 1,

Low lattice thermal conductivity is the second desired property for a high-y,-value material and the question arises how to select compounds with a good chance to have low lattice thermal conductivity. Compounds with complex crystal structure tend to have low lattice thermal conductivity. Thus, one should look for compounds with large unit cell containing a large number of atoms. Moreover, the. heavier the elements are in the compound, the lower the phonon velocity is and so is the lattice thermal conductivity. Bi_2Te_3 and PbTe are good example of heavy masses and low thermal conductivity compounds. These rules can be used to select compounds that have a good chance to have low lattice thermal conductivity.

Low (δx), heavy element compounds with complex crystal structure arc. the materials to look for with the potential for high ZT values. Of course, ZT depends on a number of other factors

but these selection criteria can be used to narrow the search. A systematic search through the periodic table of the elements led to the selection of a certain number of candidates which are listed in "l'able 1. Only binary compounds have been listed but there arc also ternary compounds or solid solutions. Compounds with relatively high melting point were first retained because our primary goal was to look for new thermoelectric materials for power generation in order to replace state-of-the-art SiGe alloys.

Table 1. Novel binary transition metal antimonides as thermoelectric materials. References for the properties can be found in [8].

Compound	T_m (c)	(δx)	Eg (eV)	Number of atoms in the unit cell	Structure
$IrSb_3$	1141	0.15	1.17	32	skutterudite
$RhSb_3$	900	0.23	-0.7	32	skutterudite
$CoSb_3$	873	0.17	0.5	32	skutterudite
$IrSb_2$	1475	0.15	?	12	arsenopyrite
$RhSb_2$	1050	0.23	?	12	arsenopyrite
$CoSb_2$	929	0.17	0.2	12	arsenopyrite
$OsSb_2$	?	0.15	?	6	marcasite
$RuSb_2$	>1250	0.2	0.26	6	marcasite

All the compounds listed in "l'able 1 have a (8x) (which was calculated using Pauling's scale) smaller than 0.25, Little information is available from the literature on the electrical properties of these compounds.

$IrSb_3$, $RhSb_3$ and $CoSb_3$ arc isostructural and have the skutterudite crystal structure type. $IrSb_3$ was recently identified as a new thermoelectric material with interesting properties, in particular a hole mobility as high as 1200 $cm^2/V.s$ [9]. High mobility have also been found on hot-pressed $RhSb_3$ samples [10], These high mobilities are consistent with the fact that the bonding was determined to be predominantly covalent in these compounds [11]. The second family of compounds listed in "1'able 1 have the arsenopyrite crystal structure type: $IrSb_2$, $RhSb_2$ and $CoSb_2$. The peritectic decomposition temperature of $IrSb_2$ was recently estimated at 1475°C in a study of the Ir-Sb phase

diagram on the antimony-rich part 112]. The band gap of $CoSb_2$ was estimated at 0.2 eV from high temperature electrical resistivity measurement [13] but no information about these compounds carrier mobility, effective mass and thermal conductivity can be found in the literature. Finally, two compounds having the marcasite crystal structure type were retained. 'l'he phase diagram of the Ru-Sb was recently determined cm the antimony-rich part and the existence of the compound $RuSb_2$, having a melting point higher than 1250°C, was confirmed [14]. Very little is known about the compound $OsSb_2$. All these promising materials are currently investigated at JPL. The following sections describe the experimental techniques and results achieved to date on some of these compounds.

EXPERIMENTAL

Suitable samples were prepared to evaluate their potential as thermoelectric materials. A wide variety of preparation techniques for bulk materials is available at JPL. Facilities for materials synthesis include several Bridgman-gradient freeze furnaces, traveling solvent method furnaces, high temperature isothermal furnaces, RF furnace, mechanical alloying mills, cold and hot presses. When the phase diagram is not known or the growth from the melt is not straightforward, the mechanical alloying (MA) process can be used and has been successfully used for several new high temperature thermoelectric materials [15]. MA constitutes an attractive alternative, preparing homogeneous compounds and alloys directly from solid materials without melting them. Two SPEX industries 8000 Mixer/Mill miller arc available at JPL. Bulk samples can be prepared from the milled powders either by cold-pressing and sintering or hot-pressing. An "Astro" hot-pressing furnace is available at JPL. The microstructure and composition of all prepared samples was investigated by microprobe analysis (M PA) and also X-ray diffractometr y (X RD). All prepared samples were measured for room temperature Hall effect. High temperature Hall effect and electrical resist ivit y, Seebeck coefficient and thermal conductivity were also measured on selected samples.

RESULTS ANI) DISCUSSION

Crystals of the compound $RuSb_2$ and the alloy $(Ru_{0.9}Cr_{0.1})Sb_2$ were grown by the gradient freeze technique. Some proper-(its of

these samples, measured at room temperature, are reported in Table 2. Mobility values as high as 144 $cm^2/V.s$ were measured and Seebeck coefficient as large as -340 $\mu V/K$ were achieved for the alloy $(Ru_{0.9}Cr_{0.1})Sb_2$.

"l'able 2. Room temperature properties for the compound $RuSb_2$ (RS 1, RS6) and the alloy $(Ru_{0.9}Cr_{0.1})Sb_2$ (2CRS 1, 3CRS2) : electrical resistivity (p), Hall coefficient (R_H), Hall mobility (μ_H) and Seebeck coefficient (α).

Sample	P ($m\Omega.cm$)	R_H (C/cm^3)	μ_H ($cm^2/V.s$)	α ($\mu V/K$)
RS1	13.69	1.9'7	144	-
RS6	9.624	0.597	62	-65
2CRS1	16.68	-0,45	- 9	-
3CRS2	22.81	-0.409	- 18	-340

The variations of the electrical resistivity and the Seebeck coefficient as a function of temperature arc reported in figures 2 and 3, respectively, Samples show intrinsic behavior at high temperature and a band gap of 0.26 eV was calculated for $RuSb_2$ and 0.28 eV for the alloy $(Ru_{0.9}Cr_{0.1})Sb_2$. Due to minority carriers conduction effects, the Seebeck coefficient of the samples become small for temperature higher than 200°C which is consistent with the relatively small band gap of these materials. Between room temperature and 200°C, large Seebeck coefficients were measured and low temperature measurements would be of interest to evaluate the potential of these materials in the low temperature range. A room temperature thermal conductivity of 140 mW/cm.K was measured on a $RuSb_2$ sample [16] which is rather a large value compare to thermal conductivity of Bi_2Te_3 alloys at room temperature. A decrease of the lattice thermal conductivity can likely be obtained by alloying $RuSb_2$ with isostructural compounds such $OsSb_2$ or $CrSb_2$ although a decrease in the carrier mobility would be expected. Preliminary results obtained on unoptimized samples suggest that some of the compounds and alloys having the marcasite structure might be useful thermoelectrics at low temperature if their thermal conductivity can be lowered through solid solution formation.

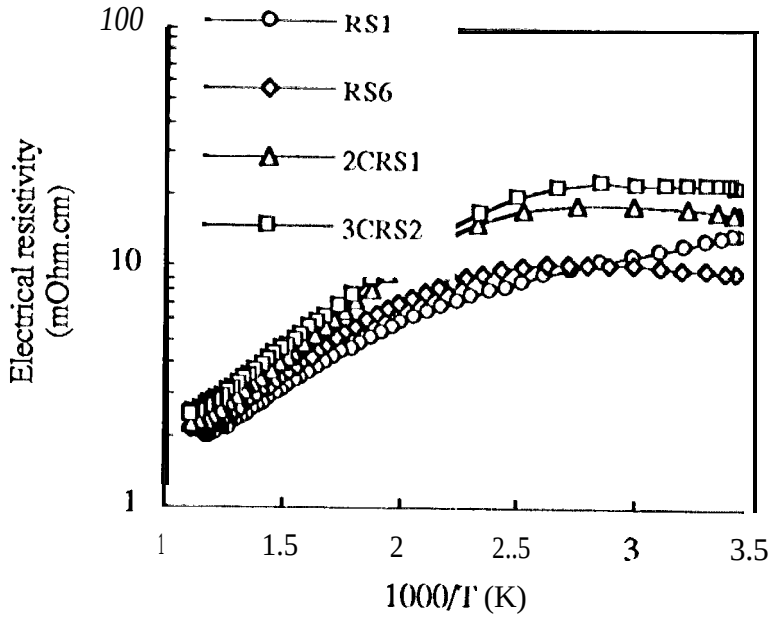

Figure 2. Electrical resistivity as a function of temperature for $RuSb_2$ samples (RS1, RS6) and samples of the alloy $(Ru_{0.9}Cr_{0.1})Sb_2$ (2CRS 1, 3CRS2).

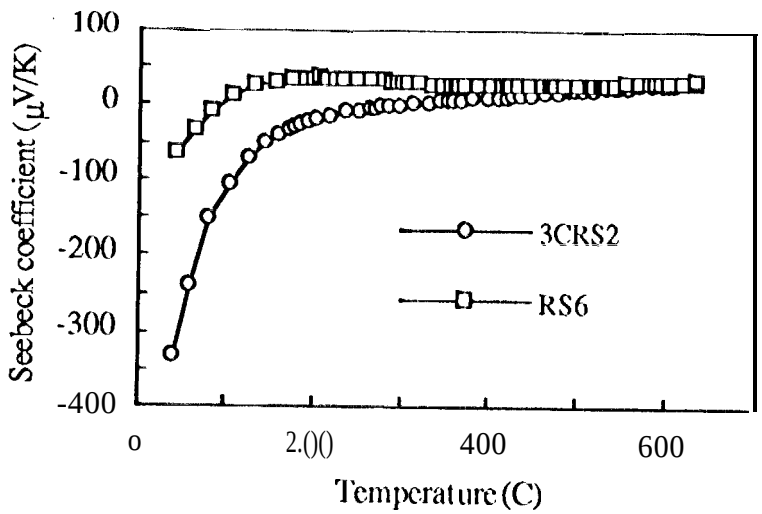

Figure 3. Seebeck coefficient as a function of temperature for $RuSb_2$ samples (RS1, RS6) and samples of the alloy $(Ru_{0.9}Cr_{0.1})Sb_2$ (2CRS 1, 3CRS2).

"l'he preparation and characterization of the compounds with the arsenopyrite crystal structure listed in Table 1 has been started

only recently and little data are now available, However, on the basis of Seebeck coefficient and electrical resistivity measurements, it has been established for the first time that $IrSb_2$ is a semiconductor. Seebeck coefficient as large as 350 μV/k were measured on several samples, The thermoelectric properties of $IrSb_2$ and isostructural compounds will be investigated in the future.

Among the materials listed in Table 1, compounds with the skutterudite structure type arc particularly promising. Figure 3 shows the dimensionless figure of merit measured on several p-typc $IrSb_3$ samples with different doping levels. Maximum ZT values for p-type Bi_2Te_3, PbTe, TAGS ('l'e, Ag, Ge, Sb) and SiGe alloys are also shown for comparison.

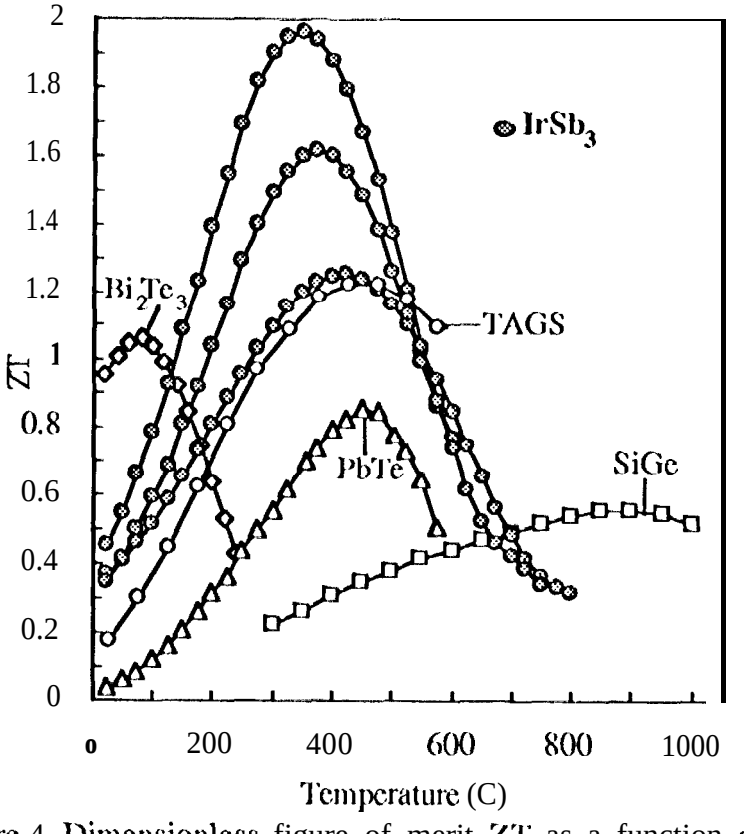

Figure 4. Dimensionless figure of merit ZT as a function of temperature for several p-type $IrSb_3$ samples with different doping levels.

A maximum ZT of 2 was achieved for the compound $IrSb_3$ in the 300-400°C temperature range which is more than twice the

performance of PbTe-based alloys commonly used in the intermediate temperature range. An average ZT value close to 1.6 was calculated over the temperature range 200-600°C which gives a material conversion efficiency of about 13%..

Although the reasons of such high ZT values have not been fully investigated yet, several factors contribute obviously to these remarkable properties. First, the therms] conductivity of $IrSb_3$ was found to be as low as 30 mW/cm.K [9]. Figure 5 shows the typical variations of the thermal conductivity as a function of the temperature for an $IrSb_3$ sample and also for PbTe and SiGe alloys. The low thermal conductivity measured for $IrSb_3$ appears to be related to the structure of the material. Indeed, $IrSb_3$ has 32 atoms per unit cell and a relatively large unit cell, both of them contribute to the low lattice thermal conductivity observed in this compound.

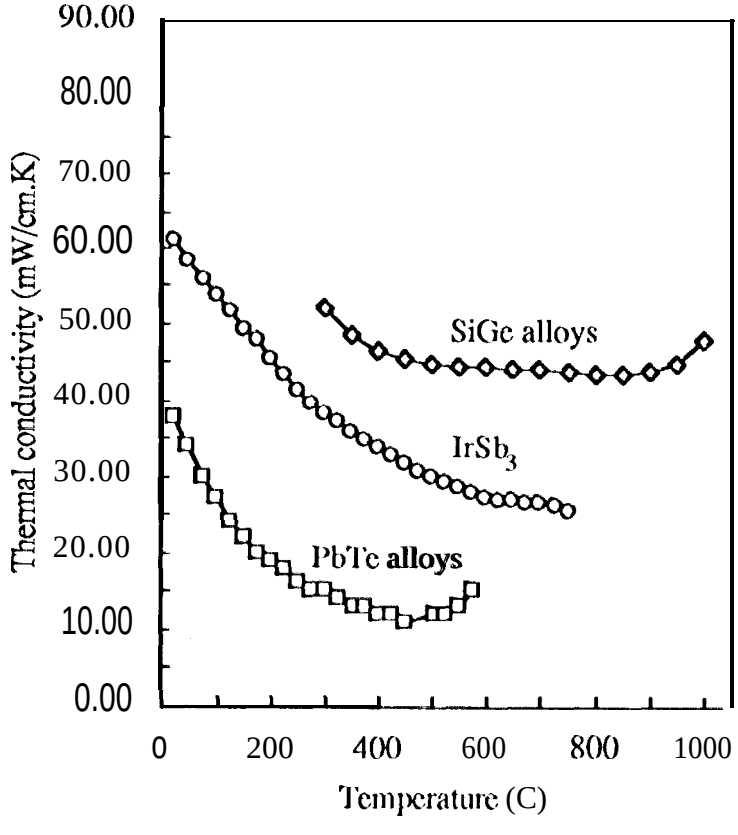

Figure 5. Thermal conductivity as a function of the temperature for several p-$IrSb_3$ samples with different doping levels and also PbTe, SiGe and Bi_2Te_3 alloys.

The second reason for the high ZT values of $IrSb_3$ is the high mobility values achieved for this compound. Room temperature mobility as high as 1250 $cm^2/V.s$ were measured on a sample with a hole concentration of 1.5 x $10^{19}.cm^{-3}$. These high mobility values also seem to be linked to the skutterudite structure. Thisstructure is composed of a cubic lattice of metal atoms and four-membered planary rings of the non-metal atoms, Band structure calculation performed on closely related compounds such as $LaFe_4P_{12}$ showed that the valence band is only made from P-P bonds [17] and it is likely that the valence band of $IrSb_3$ can be formed from Sb-Sb bonds. The high mobility values can be related to this particular valence band feature and also to the covalency of the skutterudite structure. In summary, high ZT values for $IrSb_3$ seem to be primarily related to its low lattice thermal conductivity and high mobility.

The remarkable properties of the compound $IrSb_3$ arc also well illustrated on figure 6 where the calculated power factor-s ($\alpha^2\sigma$) for several $IrSb_3$ samples with different doping levels arc plotted as a function of the temperature. Compare to state-of-the-art thermoelectric materials like Bi_2Te_3, PbTe and SiGe alloys, exceptionally high values were obtained for the $IrSb_3$.

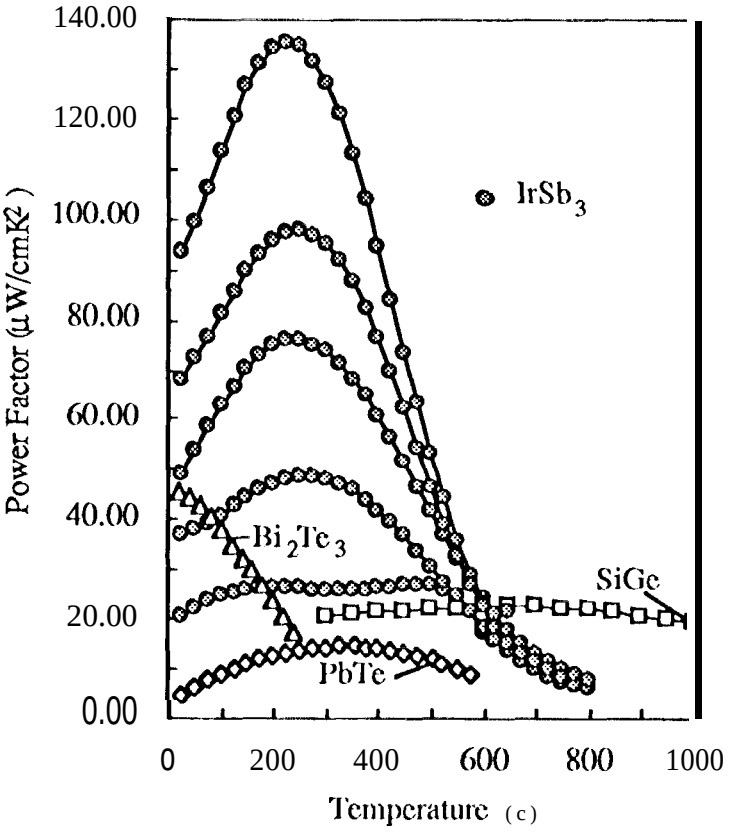

Figure 6. Power factor as a function of the temperature for several p-$IrSb_3$ samples with different doping levels and also PbTe, SiGe and Bi_2Te_3 alloys,

CONCLUSION

This paper described the successful approach conducted at JPL for a search for new thermoelectric materials with the potential to overcome the ZT limit of 1. Indeed, experimental results obtained for the compound $IrSb_3$ have shown that ZTs' as high as 2. were achieved. Other low (δx), heavy elements binary compounds with complex crystal structure remain to be investigated and have also the potential to be high-Z-values materials and the number of candidates can be i ncrcascd by considering ternary compounds and alloys.

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